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Reactions of Pyrazolo[1,5-*a*]pyrimidine Derivatives with Nucleophiles. I. Nucleophilic Addition to 6,7-Dicarbethoxypyrazolo[1,5-*a*]-pyrimidine-3-carbonitrile in the Presence of Boron Trifluoride Etherate

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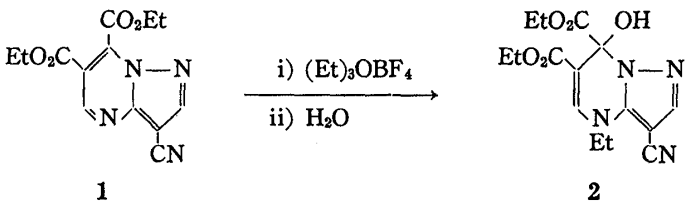
Nucleophilic additions of phenol analogs, indoles, and enamines of cyclohexanone to 6,7-dicarbethoxypyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1**) in the presence of boron trifluoride etherate are described. For example, though phenol or *o*-cresol (having no substituent at the *para*-position) reacted with **1** to give cyclohexadienylidene derivatives (**3**, **4**), *p*-cresol or *p*-methoxyphenol gave the spiro{benzofuran-3(2H),7′(4′H)-pyrazolo-[1,5-*a*]pyrimidine} compounds (**6**, **7**) upon reaction with **1**. Indoles reacted with **1** to give the 7-indolyl derivatives (**11**, **12**). When **1** was treated with enamines of cyclohexanone in the presence of a slight excess of boron trifluoride etherate, 7-(2-amino-1-cyclohexenyl)pyrazolo[1,5-*a*]pyrimidines (**13**, **14**) were obtained as their boron trifluoride complexes in good yields.

Keywords——pyrazolo[1,5-*a*]pyrimidine; phenol; α- and β-naphthol; indole; enamine; boron trifluoride etherate; spiro{benzofuran-3(2H),7′(4′H)-pyrazolo[1,5-*a*]-pyrimidine}; spiro{naphtho[1,2-*b*]furan-3(2H),7′(4′H)-pyrazolo[1,5-*a*]pyrimidine}; spiro-{naphtho[2,1-*b*]furan-3(2H),7′(4′H)-pyrazolo[1,5-*a*]pyrimidine}; spiro lactone

The reactivity of azine, benzoazine and azinoazine derivatives with simple nucleophiles has been widely investigated.[1] It is known that the reactions of N-alkylated or arylated azinium compounds with nucleophiles proceed more readily than those of the parent, uncationated azines.[2] The formation of 2-quinolones from quinoline quaternary salts is also well known, but usually a good leaving group in another strongly activated position is not present.[3] For example, Schock reported[4] that upon treatment of 1-methyl-4,7-dichloroquinolinium ion with cold alkali, about 20% of the 2-hydroxylation product was isolated in addition to 35% of the 1-methyl-4-quinolone formed by displacement of the highly reactive 4-chloro group.

We have recently reported the preparation and chemical reactivity (*e.g.*, catalytic hydrogenation, reaction with diazomethane and its analog, reaction with phenylhydrazine, *etc.*) of 6,7-dicarbethoxypyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1**) and its analogs.[5] Quite recently, we found that treatment of **1** with triethyl oxoniumfluoroborate, which is known to convert pyrimidines to diquaternary salts,[6] followed by treatment with cold water gave 6,7-dicarbethoxy-4,7-dihydro-4-ethyl-7-hydroxypyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2**)[7] in 55% yield.

In connection with this result, we would now like to describe some reactions of **1** with several nucleophiles in the presence of boron trifluoride etherate ($BF_3 \cdot Et_2O$) instead of triethyl oxoniumfluoroborate.



1 **2**

Chart 1

Reactions with Phenol Analogs

First, nucleophilic addition of **1** with phenol was investigated. When a mixture of **1** and 3 equivalents of phenol was refluxed with a limited amount of $BF_3 \cdot Et_2O$ in dichloromethane, diethyl 2-(4-oxo-2,5-cyclohexadienylidene)-3-(4-cyano-3-pyrazolylamino)methylenesuccinate (**3**),[8] $C_{19}H_{18}N_4O_5$, mp 214—215°C, was obtained in quantitative yield. The infrared (IR) spectrum of **3** showed strong absorption bands at 1750, 1680 (CO), and 1600 (C=C) cm^{-1}. The nuclear magnetic resonance (NMR) spectrum of **3** showed characteristic AB quartet signals at δ 6.65 and 7.01 ppm (each 2H, each d, $J=9$ Hz) as well as an olefinic proton signal at δ 7.56 ppm and a pyrazole ring proton signal at δ 7.93 ppm. However, **3** did not give a positive ferric chloride test {$FeCl_3$–$K_3[Fe(CN)_6]$}. Based on these results, the cyclohexadienone structure (**3**) was assigned to this product, presumably formed *via* the addition product 3′. Thus, this product was treated with acetic anhydride containing a catalytic amount of sulfuric acid, and 7-(*p*-acetoxyphenyl)-6,7-dicarbethoxy-4,7-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5**) was successfully obtained in 88% yield. The NMR signals due to the acetoxyphenyl moiety of **5** [δ 7.05 and 7.25 ppm (each 2H, each d, $J=9$ Hz, aromatic H) and δ 2.26 ppm (3H, s, $OCOCH_3$)] are in fair agreement with the data (DMSO-d_6) for *p*-acetoxytoluene [δ 6.95 and 7.20 ppm (each 2H, each d, $J=9$ Hz, aromatic H) and δ 2.26 ppm (3H, s, $OCOCH_3$)].

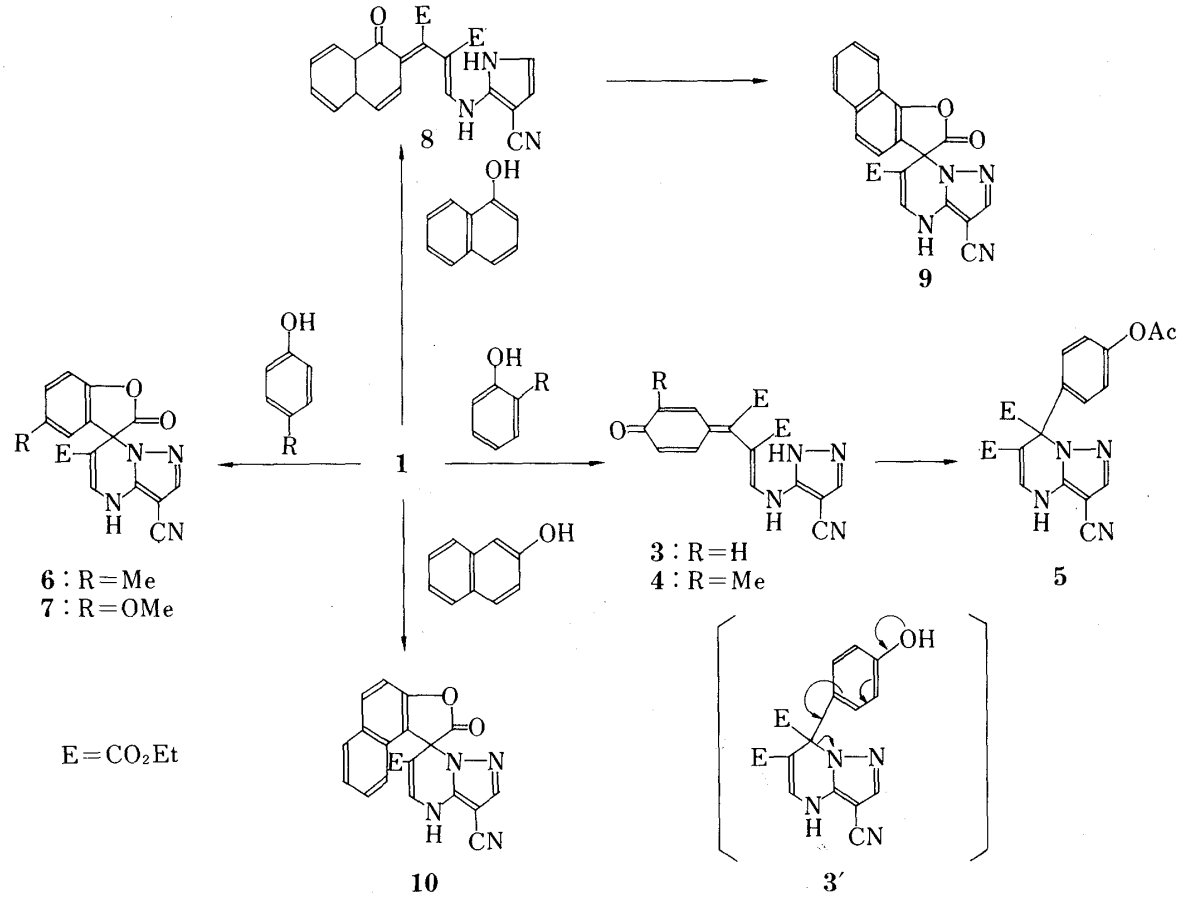


Chart 2

Similarly, by the treatment of **1** with *o*-cresol, a product (**4**) was obtained in 27.6% yield. Treatment of **1**, however, with 1.5 equivalents of *p*-cresol in the presence of $BF_3 \cdot Et_2O$ gave a crystalline product, $C_{18}H_{14}N_4O_4$, mp 273—275°C, in 34.4% yield. Based on the spectral data, the spiro{benzofuran-3(2H),7′(4′H)-pyrazolo[1,5-*a*]pyrimidine}-2-one structure (**6**) was assigned to this product. Thus, in the IR spectrum an absorption band due to γ-lactone

appeared at 1810 cm^{-1}. In the NMR spectrum, signals due to one-$CO_2CH_2CH_3$ group [δ 1.06 ppm (3H, t) and 3.96 ppm (2H, q)] were observed, together with two singlets due to C(2')- and/or C(5')-protons at δ 7.78 and 7.90 ppm. Moreover, the ultraviolet (UV) spectrum showed an absorption maximum at 316 nm (4.18), which is very similar to that of the 4,7-dihydro derivatives of **1**.[5] Under the same experimental conditions as above, *p*-methoxyphenol and β-naphthol were treated with **1** to give the corresponding spiro lactones (**7** and **10**) in 36.9 and 31.4% yields, respectively. The analytical and IR spectral data for the spiro lactones are summarized in Table I.

TABLE I. Analytical and IR Spectral Data for Spiro Lactone Derivatives

Compd. No.	mp (°C)	Yield (%)	Formula	Analyses (%) Calcd (Found) C	H	N	IR ν_{max}^{KBr} cm^{-1} (NH)	(CN)	(CO)
6	273—275[a]	34.4	$C_{18}H_{14}N_4O_4$	61.71	4.03	16.00	3210	2220	1810
				(61.76	3.94	16.02)			1700
7	253—254[a]	36.9	$C_{18}H_{14}N_4O_5$	59.01	3.85	15.30	3120	2220	1820
				(58.80	3.85	15.05)			1690
9	>300[b]	24.9[c]	$C_{21}H_{14}N_4O_4$	65.28	3.65	14.50	3220	2220	1820
				(65.52	3.84	14.63)			1700
10	>300[a]	31.4	$C_{21}H_{14}N_4O_4$	65.28	3.65	14.50	3210	2220	1820
				(65.03	3.60	14.50)			1680

a) Recrystallized from EtOH.
b) Recrystallized from CH_3CN–H_2O.
c) Total yield from **1**.

In contrast to the reaction of **1** with β-naphthol, the reaction of **1** with α-naphthol by the same procedure afforded diethyl 2-(1,2-dihydro-1-oxo-2-naphthylidene)-3-(4-cyano-3-pyrazolylamino)methylenesuccinate (**8**), $C_{23}H_{20}N_4O_5$, mp 212—213°C, in 40.7% yield. Evidence for this structure was provided by the IR spectrum (in which no absorption band due to γ-lactone appeared), the NMR spectrum (in which signals due to two $-CO_2CH_2CH_3$ groups appeared), and the negative $FeCl_3$–$K_3[Fe(CN)_6]$ test. As expected, the spiro compound **9** (Table I) was obtained readily when **8** was refluxed in ethanol in the presence of hydrochloric acid.

Reactions with Indoles

Treatment of **1** with 2.5 equivalents of indole in dichloromethane in the presence of a catalytic amount of $BF_3 \cdot Et_2O$ at room temperature resulted in the formation of 6,7-dicarbethoxy-4,7-dihydro-7-(3-indolyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**11**) in 96.9% yield. The structure was assigned on the bases of the results of elemental analysis, and the spectral data [signals at δ 7.60 and 7.83 ppm due to C(2)- and C(5)-protons in the NMR spectrum and an absorption maximum at 316 nm (4.19) in the UV spectrum]. Under the same conditions, 1-methylindole reacted with **1** to give the 7-indolyl derivative (**12**) in fairly good yield.

Reactions with Enamines of Cyclohexanone

Hamana *et al.*[9] reported that aromatic N-oxides react with enamines of cyclohexanone in the presence of acylating agents. It is also known that N-alkoxyquinolinium salts react with 1-morpholinocyclohexene without any catalyst.[10] Thus, the diester (**1**) was allowed to react with 3.0 equivalents of 1-morpholinocyclohexene in the presence of a slight excess of $BF_3 \cdot Et_2O$ under ice cooling. Subsequently the reaction mixture was shaken with cold water, and a crystalline product (**13**), mp 154—155°C, which gave a positive Beilstein test, was isolated in a yield of 94.1%. Elemental analysis of **13** established its molecular formula to be $C_{23}H_{29}N_5O_5BF_3$. The NMR spectrum of **13** suggested the presence of a 1-morpholinocyclohex-

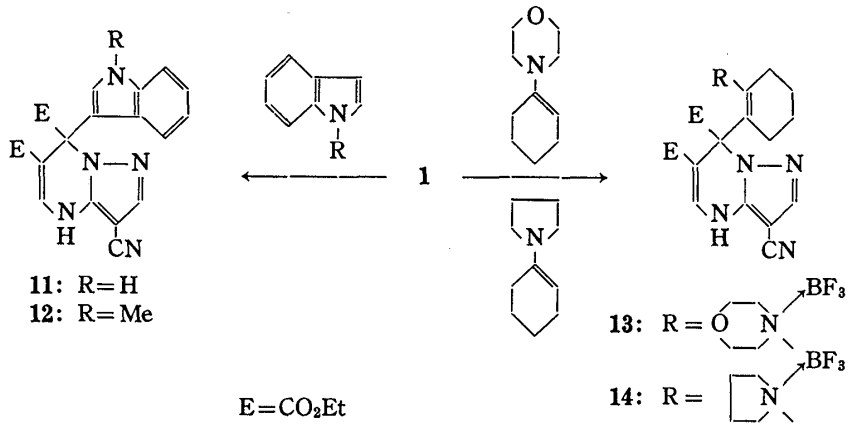


Chart 3

enyl moiety in the molecule,[11] and there were two singlet signals at δ 7.85 and 8.00 ppm due to C(5)- and C(2)-protons. On the basis of these results, **13** was assigned as the boron trifluoride complex of 6,7-dicarbethoxy-4,7-dihydro-7-(2-morpholino-1-cyclohexenyl)pyrazolo[1,5-*a*]-pyrimidine-3-carbonitrile.

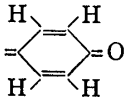
Treatment of this complex with 20% hydrochloric acid decomposed it to give **1** unexpectedly. The reaction of **1** with 1-pyrrolidinocyclohexene progressed smoothly and resulted in the formation of **14** in good yield.

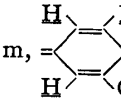
Further experiments on the reaction of **1** with various other kinds of nucleophiles are under way.

Experimental

All melting points were recorded on a Yanagimoto melting point apparatus and are uncorrected. The IR spectra were recorded with a JASCO IRA-1 spectrophotometer, and the UV spectra with a JASCO UVIDEC-505 spectrophotometer. The NMR spectra were recorded with a Hitachi R-24A spectrometer with tetramethylsilane as an internal standard.

Reaction of 1 with Phenol or *o*-Cresol——Three drops of $BF_3 \cdot Et_2O$ were added to a solution of 1 mmol of 1 and 3 mmol of phenol or *o*-cresol in 50 ml of dry CH_2Cl_2, and the mixture was refluxed for 24 h. After removal of the solvent by evaporation, EtOH was added to the residue and the resulting crystalline solid was collected by filtration and purified by recrystallization.

Diethyl 2-(4-Oxo-2,5-cyclohexadienylidene)-3-(4-cyano-3-pyrazolylamino)methylenesuccinate (3)—100% yield. mp 214—215°C (AcOEt: *n*-hexane). IR ν_{max}^{KBr} cm^{-1}: 3350 (NH), 2220 (CN), 1750, 1680 (CO), 1600 (C=C). NMR (DMSO-d_6) δ: 1.00—1.30 (6H, m, $2\times CO_2CH_2\underline{CH_3}$), 3.90—4.43 (4H, m, $2\times CO_2\underline{CH_2}CH_3$), 6.65 and 7.01 (each 2H, each d, J=9 Hz, ), 7.56 (1H, s, =CH), 7.93 (1H, s, pyrazole ring-H), 9.48 (1H, s, NH), 11.65 (1H, bs, NH). UV λ_{max}^{EtOH} nm (log ε): 226 (4.16), 284 (sh) (3.83), 315 (4.20). *Anal.* Calcd for $C_{19}H_{18}N_4O_5$: C, 59.68; H, 4.75; N, 14.65. Found: C, 59.79; H, 4.59; N, 14.55.

Diethyl 2-(3-Methyl-4-oxo-2,5-cyclohexadienylidene)-3-(4-cyano-3-pyrazolylamino)methylenesuccinate (4)——27.6% yield. mp 217—219°C (AcOEt). IR ν_{max}^{KBr} cm^{-1}: 3380 (NH), 2220 (CN), 1740, 1690 (CO), 1600 (C=C). NMR (DMSO-d_6) δ: 1.00—1.30 (6H, m, $2\times CO_2CH_2\underline{CH_3}$), 2.07 (3H, s, CH_3), 3.97—4.30 (4H, m, $2\times CO_2\underline{CH_2}CH_3$), 6.58—7.02 (3H, m, ), 7.58 (1H, s, =CH), 7.95 (1H, s, pyrazole ring-H), 9.39 (1H, s, NH), 11.45 (1H, bs, NH). *Anal.* Calcd for $C_{20}H_{20}N_4O_5$: C, 60.60; H, 5.09; N, 14.14. Found: C, 60.59; H, 5.09; N, 14.14.

7-(*p*-Acetoxyphenyl)-6,7-dicarbethoxy-4,7-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (5)——One drop of conc. H_2SO_4 was added to a suspension of 350 mg of 3 in 10 ml of acetic anhydride, and the mixture was stirred for 0.5 h at room temperature. The solution was poured into ice-water, made alkaline with $NaHCO_3$, and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water and dried over Na_2SO_4. After removal of the solvent, EtOH was added to the residue and the resulting crystalline solid was collected by filtration to give 375 mg (88%) of **5**. mp 182—183°C (AcOEt: *n*-hexane). IR ν_{max}^{KBr} cm^{-1}: 2220 (CN),

1750, 1690 (CO). NMR (DMSO-d_6) δ: 1.02—1.30 (6H, m, $2\times CO_2CH_2C\underline{H}_3$), 2.26 (3H, s, $OCOCH_3$), 4.00—4.32 (4H, m, $2\times CO_2C\underline{H}_2CH_3$), 7.05 and 7.25 (each 2H, each d, $J=9$ Hz, Ar–H), 7.65 [1H, s, C(5)–H], 8.02 [1H, s, C(2)–H]. UV λ_{max}^{EtOH} nm (log ε): 314 (4.19). *Anal.* Calcd for $C_{21}H_{20}N_4O_6$: C, 59.43; H, 4.75; N, 13.20. Found: C, 59.73; H, 4.59; N, 13.44.

6′-Carbethoxy-3′-cyano-5-methylspiro{benzofuran-3(2H),7′(4′H)-pyrazolo[1,5-*a*]pyrimidine}-2-one (6)——From 1 mmol of **1** and 1.5 mmol of *p*-cresol, 110 mg (31.4%) of **6** (Table I) was obtained by the method described for the preparation of **3** (or **4**). NMR (DMSO-d_6) δ: 1.06 (3H, t, $J=7$ Hz, $CO_2CH_2C\underline{H}_3$), 3.96 (2H, q, $J=7$ Hz, $CO_2C\underline{H}_2CH_3$), 7.03—7.23 (3H, m, Ar–H), 7.78 and 7.90 [each 1H, each s, C(2′)- and/or C(5′)–H]. UV λ_{max}^{EtOH} nm (log ε): 316 (4.18), 368 (3.66).

6′-Carbethoxy-3′-cyano-5-methoxyspiro{benzofuran-3(2H),7′(4′H)pyrazolo[1,5-*a*]pyrimidine}-2-one (7)——To a solution of 1 mmol of **1** and 1.5 mmol of *p*-methoxyphenol in 50 ml of dry CH_2Cl_2 was added 0.3 ml of $BF_3\cdot Et_2O$, and the mixture was refluxed for 4 days. After remaval of the solvent by evaporation, the residue was subjected to silica gel column chromatography. The first fraction eluted with $CHCl_3$ was yielded 60 mg (20.8%) of **1**. The last fraction eluted with $CHCl_3$–MeOH (29: 1) gave 135 mg (36.9%) of **7** (Table I). NMR (DMSO-d_6) δ: 1.09 (3H, t, $J=7$ Hz, $CO_2CH_2C\underline{H}_3$), 3.69 (3H, s, OCH_3), 4.00 (2H, q, $J=7$ Hz, $CO_2C\underline{H}_2CH_3$), 6.88—7.30 (3H, m, Ar–H), 7.82 and 7.95 [each 1H, each s, C(2′)- and/or C(5′)–H], 12.00 (1H, bs, NH).

Diethyl 2- (1,2-Dihydro-1-oxo-2-naphthylidene) -3- (4-cyano-3-pyrazolylamino) methylenesuccinate (8)——A few drops of $BF_3\cdot Et_2O$ were added to a solution of 1 mmol of **1** and 1.5 mmol of α-napthol in 50 ml of dry CH_2Cl_2, and the mixture was refluxed for 24 h. The resulting precipitate was collected by filtration and washed with CH_2Cl_2 to give 176 mg (40.7%) of **8**. mp 212—213°C (EtOH). IR ν_{max}^{KBr} cm^{-1}: 3200 (NH), 2220 (CN), 1740, 1680 (CO). NMR (DMSO-d_6) δ: 0.90—1.30 (6H, m, $2\times CO_2CH_2C\underline{H}_3$), 3.92 and 4.16 (each 2H, each q, $J=7$ Hz, $2\times CO_2C\underline{H}_2CH_3$), 7.20—8.20 (8H, m, Ar–H, =CH, and pyrazole ring-H) 9.55 (1H, s, NH), 11.62 (1H, bs, NH). UV λ_{max}^{EtOH} nm (log ε): 236 (4.29), 313 (4.14). *Anal.* Calcd for $C_{23}H_{20}N_4O_5$: C, 63.88; H, 4.66; N, 12.96. Found: C, 64.03; H, 4.54; N, 12.87.

6′-Carbethoxy-3′-cyanospiro{naphto[1,2-*b*]furan-3(2H),7′(4′H)-pyrazolo[1,5-*a*]pyrimidine}-2-one (9)——A solution of 115 mg of **8** and 0.5 ml of conc. HCl in 50 ml of EtOH was refluxed for 24 h. After removal of the solvent by evaporation, the resulting precipitate was collected by filtration and purified by recrystallization to give 63 mg (61.3%) of **9** (Table I). NMR (DMSO-d_6) δ: 1.00 (3H, t, $J=7$ Hz, $CO_2CH_2C\underline{H}_3$), 3.92 (2H, q, $J=7$ Hz, $CO_2C\underline{H}_2CH_3$), 7.30—8.15 [8H, m, Ar–H, C(2′)- and C(5′)–H], 12.30 (1H, bs, NH). UV λ_{max}^{EtOH} nm (log ε): 316 (4.22), 328 (sh) (4.16), 375 (sh) (3.64).

6′-Carbethoxy-3′-cyanospiro{naphtho[2,1-*b*]furan-3(2H),7′(4′H)pyrazolo[1,5-*a*]pyrimidine}-2-one (10)——Three drops of $BF_3\cdot Et_2O$ were added to a solution of 1 mmol of **1** and 1.5 mmol of β-naphthol in 50 ml of dry CH_2Cl_2, and the mixture was refluxed for 24 h, then cooled. The precipitate was collected by filtration to give 132 mg (34.2%) of **10** (Table I), which was purified by recrystallization. NMR (DMSO-d_6) δ: 1.11 (3H, t, $J=7$ Hz, $CO_2CH_2C\underline{H}_3$), 3.93 (2H, q, $J=7$ Hz, $CO_2C\underline{H}_2CH_3$), 7.15—8.25 [8H, m, Ar–H, C(2′)- and C(5′)–H].

General Procedure for the Reaction of 1 with Indoles——A catalytic amount of $BF_3\cdot Et_2O$ was added to a solution of 1 mmol of **1** and 2.5 mmol of an indole in 15 ml of dry CH_2Cl_2 at room temperature. The resulting precipitate was collected by filtration, washed with cold EtOH, and purified by recrystallization.

6,7-Dicarbethoxy-4,7-dihydro-7-(3-indolyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (11)——96.9% yield. mp 265—267°C (EtOH). IR ν_{max}^{KBr} cm^{-1}: 3400 (NH), 2220 (CN), 1750, 1700 (CO), 1600 (C=C). NMR (DMSO-d_6) δ: 1.13 (6H, t, $J=7$ Hz, $2\times CO_2CH_2C\underline{H}_3$), 3.90—4.30 (4H, m, $2\times CO_2C\underline{H}_2CH_3$), 6.90—7.30 (4H, m, Ar–H), 7.60 [2H, s, C(5)–H, and C(2)–H of indole ring], 7.83 [1H, s, C(2)–H], 11.50 (1H, s, NH), 12.00 (1H, bs, NH). UV λ_{max}^{EtOH} nm (log ε): 282 (sh) (4.01), 288 (4.04), 316 (4.19). *Anal.* Calcd for $C_{21}H_{19}N_5O_4$: C, 62.21; H, 4.72; N, 17.28. Found: C, 62.21; H, 4.70; N, 17.01.

6,7-Dicarbethoxy-4,7-dihydro-7-(N-methyl-3-indolyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (12)——81.5% yield. mp 275—277°C (EtOH). IR ν_{max}^{KBr} cm^{-1}: 2220 (CN), 1750, 1700 (CO), 1600 (C=C). NMR (DMSO-d_6) δ: 1.10 (6H, t, $J=7$ Hz, $2\times CO_2CH_2C\underline{H}_3$), 3.73 (3H, s, NCH_3), 3.85—4.30 (4H, m, $2\times CO_2C\underline{H}_2CH_3$), 6.80—7.40 (4H, m, Ar–H), 7.60 [2H, s, C(5)–H, and C(2)–H of indole ring], 7.80 [1H, s, C(2)–H]. *Anal.* Calcd for $C_{22}H_{21}N_5O_4$: C, 63.00; H, 5.05; N, 16.70. Found: C, 62.72; H, 5.03; N, 16.94.

General Procedure for the Reaction of 1 with Enamines of Cyclohexanone——To a solution of 2 mmol of **1** and 4 mmol of 1-morpholino- or pyrrolidino-cyclohexane in 50 ml of dry CH_2Cl_2 was added 1 ml of $BF_3\cdot Et_2O$ under ice cooling. After standing at room temperature for 10 min, the solution was washed with cold water. The CH_2Cl_2 layer was dried over Na_2SO_4 and evaporated to dryness. The resulting solid was purified by recrystallization.

Boron Trifluoride Complex of 6,7-Dicarbethoxy-4,7-dihydro-7-(2-morpholino-1-cyclohexenyl)pyrazolo-[1,5-*a*]pyrimidine-3-carbonitrile (13)——94.1% yield. mp 153—154°C (CH_3CN). IR ν_{max}^{KBr} cm^{-1}: 3450 (NH), 2220 (CN), 1750, 1710 (CO), 1620 (C=C). NMR (DMSO-d_6) δ: 7.85 [1H, s, C(5)–H], 8.00 [1H, s, C(2)–H]. *Anal.* Calcd for $C_{23}H_{29}N_5O_5BF_3$: C, 52.78; H, 5.58; N, 13.38. Found: C, 52.86; H, 5.76; N, 13.37.

Boron Trifluoride Complex of 6,7-Dicarbethoxy-4,7-dihydro-7-(2-pyrrolidino-1-cyclohexenyl)pyrazolo-[1,5-*a*]pyrimidine-3-carbonitrile (14)——92.0% yield. mp 171—173°C (CH_3CN). IR ν_{max}^{KBr} cm^{-1}: 3450 (NH), 2220 (CN), 1750, 1690 (CO), 1620 (C=C). NMR (DMSO-d_6) δ: 7.85 [1H, s, C(5)–H], 8.00 [1H, s, C(2)–H]. *Anal.* Calcd for $C_{23}H_{29}N_5O_4BF_3$: C, 54.45; H, 5.76; N, 13.80. Found: C, 54.64; H, 5.85; N, 13.63.

Treatment of 13 with 20% Hydrochloric Acid——A suspension of 1 mmol of **13** in 20 ml of 20% HCl was stirred at room temperature until all of **13** had dissolved. The solution was concentrated *in vacuo* at 40°C, then the residue was neutralized with saturated $NaHCO_3$ solution and extracted with $CHCl_3$. The $CHCl_3$ layer was dried over Na_2SO_4, and evap orated to dryness to give a crystalline solid, which was recrystallized from EtOH to give 75 mg of **1**.

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References and Notes

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